

On the influence of the electrode and chaotropicity of the electrolyte on the oscillatory behavior of the electrocatalytic oxidation of SO₂

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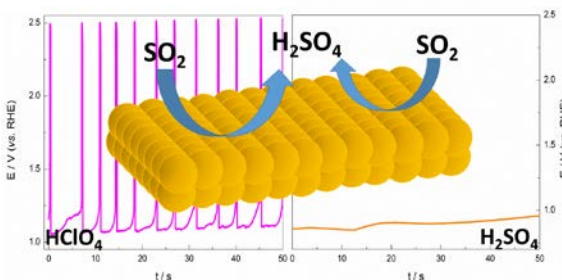
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ABSTRACT

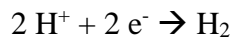
SO₂ oxidation has been proposed as an alternative pathway for the electrochemical generation of H₂ as it requires lower potentials than water splitting and at the same time consumes an atmospheric pollutant. Theoretical predictions suggest that gold and platinum are the most active catalysts for this reaction. This work presents experimental evidence that, contrary to the predictions, SO₂ oxidation starts at less positive potentials on Au electrodes (*ca.* 0.60 V (*vs.* RHE)) than on Pt. It is found further that the observed current densities on Au are one order of magnitude higher than on Pt. In addition, the SO₂ oxidation mechanism depends on the chemical nature of the electrolyte used: a kosmotropic anion (HSO₄⁻) results in lower currents than a chaotropic one (ClO₄⁻) and the latter displays oscillatory reaction rates under both potentiostatic and galvanostatic regimes.

TOC GRAPHICS



INTRODUCTION

The hybrid sulfur cycle (HyS)¹, proposed during the 1970's², is a process in which SO₂ is oxidized to H₂SO₄, and as a counter reaction, water is reduced to H₂ (Scheme 1).



Scheme 1. Overall SO₂ oxidation reaction

The standard thermodynamic potential of this process is 0.158 V_{RHE} and thus significantly lower than the corresponding thermodynamic potential in water electrolysis (1.229 V_{RHE}³). Therefore SO₂ oxidation could be a cheaper, cleaner and more environmental friendly pathway to produce H₂, since it utilizes an atmospheric pollutant to produce a clean fuel. However, the need of a suitable catalyst for this reaction that provides a low kinetic barrier is challenging and the main motivation for studies in this field¹⁻¹³. Recent reports⁹ indicate that Au and Pt should be the most electroactive catalysts (with the order in activity Pt > Au). This mechanism is in disagreement with proposed by previous experimental reports¹¹⁻¹³. The goal of the present work was to provide experimental data of the electrochemical oxidation process on both electrodes and to confront both mechanisms.

MATERIALS AND METHODS

A two-compartment H shape electrochemical cell was used, with Pt or Au disk (d= 0.50 cm) as working electrodes, a Pt mesh and a RHE as counter and reference, respectively. The supporting electrolytes were HClO₄ and H₂SO₄ SuprapurTM 0.5 mol L⁻¹ solutions, prepared with

Milli-Q™ water. N₂ was bubbled into the solution and after 20 min, the gas was changed to SO₂ (Air Liquide) and the solution was saturated for 25 min.

The electrochemical area of the electrodes was measured by H_{upd}, in the case of Pt electrode, and Cu_{upd}, in case of Au electrode. The CuSO₄ solution was 0.10 mol L⁻¹, in H₂SO₄ 0.50 mol L⁻¹ and the deposition of a Cu monolayer is in agreement with the one proposed in the literature^{14,15}.

All experiments were performed at room temperature and controlled by an Autolab potentiostat/ galvanostat (AUT85732).

RESULTS AND DISCUSSION

To determine the potential region where the electrochemical reaction takes place, cyclic voltammograms on Au and Pt electrodes were recorded in sulfuric acid electrolyte solutions saturated with Ar and SO₂, respectively, see Figure 1.

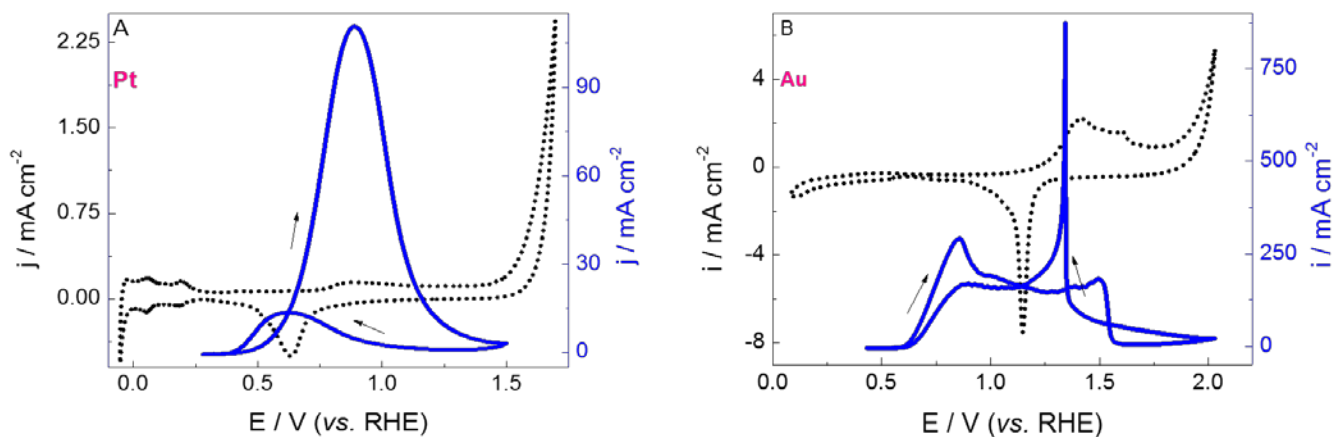
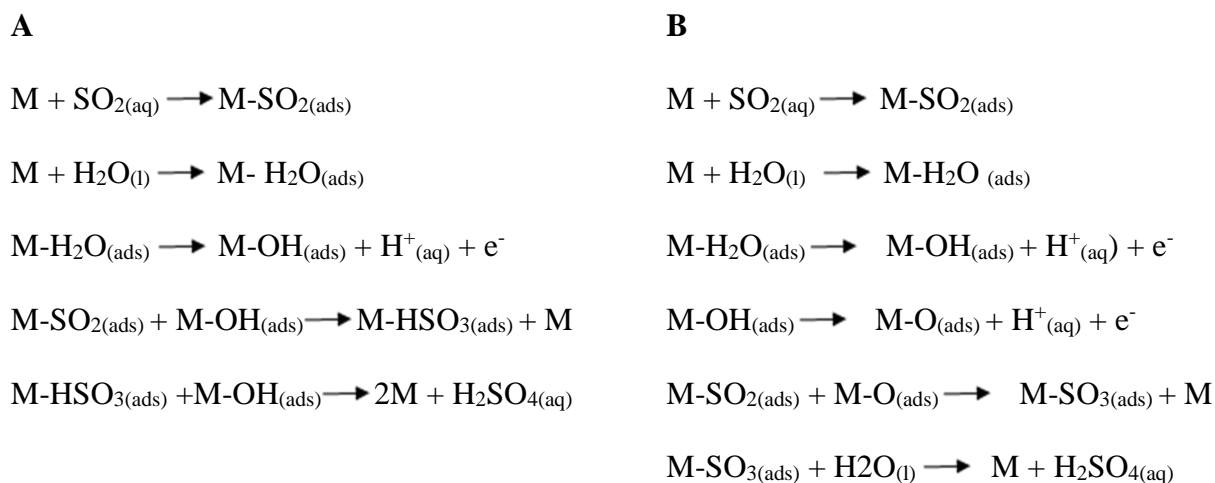


Figure 1. *j*/*E* potentiodynamic profiles of polycrystalline Pt (**A**) and Au (**B**) electrodes in the absence (black dashed lines) and in the presence (full blue line) of SO₂. Electrolytic solution: H₂SO₄ 0.5 mol L⁻¹. Scan rate: 0.1 V s⁻¹, scan direction indicated by the arrows.

Figure 1A indicates that the highest Pt catalytic activity takes place in the same potential region where oxide formation occurs, a strong evidence that the catalytic species are indeed related to those suggested previously by theoretical calculations by Kriek *et al.*⁹, **Scheme 2**.



Scheme 2. Calculated⁹ possible pathways for the SO₂ oxidation on noble metal surfaces. **A.** Metal hydroxides considered as catalytic species. **B.** Metal oxides as catalyst.

In contrast, the electrochemical behavior is completely different on Au surfaces. Figure 1B shows that the oxidation process starts at around 0.60 V_{RHE} with a peak maximum at around 0.80 V_{RHE}, i.e. at significantly lower potentials than the 1.60 V_{RHE} predicted by the calculations⁹ following **Scheme 2**. Furthermore, the current density on the Au electrode is higher than on Pt. Another striking point is the shape of the j/E profile shown in Figure 1B, i.e. a sharp oxidation peak occurs at 1.35 V_{RHE} during the negative going scan. Such a feature was already observed in previous work for high SO₂ concentrations¹⁶, but is usually not seen at low SO₂ concentration.^{17,18} During the positive going scan, the oxidation current drops to almost zero at around 1.50 V_{RHE}, in the same region where the Au surface oxide formation takes place. This suggests that adsorbed SO₂ is directly oxidized on a bare Au surface in a Langmuir-Hinshelwood step. Such reaction step is

completely different from those depicted in **Scheme 2**, where the presence of surface oxides is needed as the active species for SO₂ oxidation. Similar conclusions were obtained by O'Brien *et al.*, not only for Au electrodes¹³, but also for Pt electrodes^{11,13}, when varying the electrolyte concentration and applying a pre-treatment. To investigate the reaction further and to determine the influence of a partial blocked surface (by anions) onto the SO₂ oxidation, also suggested by previous works¹³, we compared the reaction in HClO₄ and H₂SO₄ electrolyte solutions, see Figure 2.

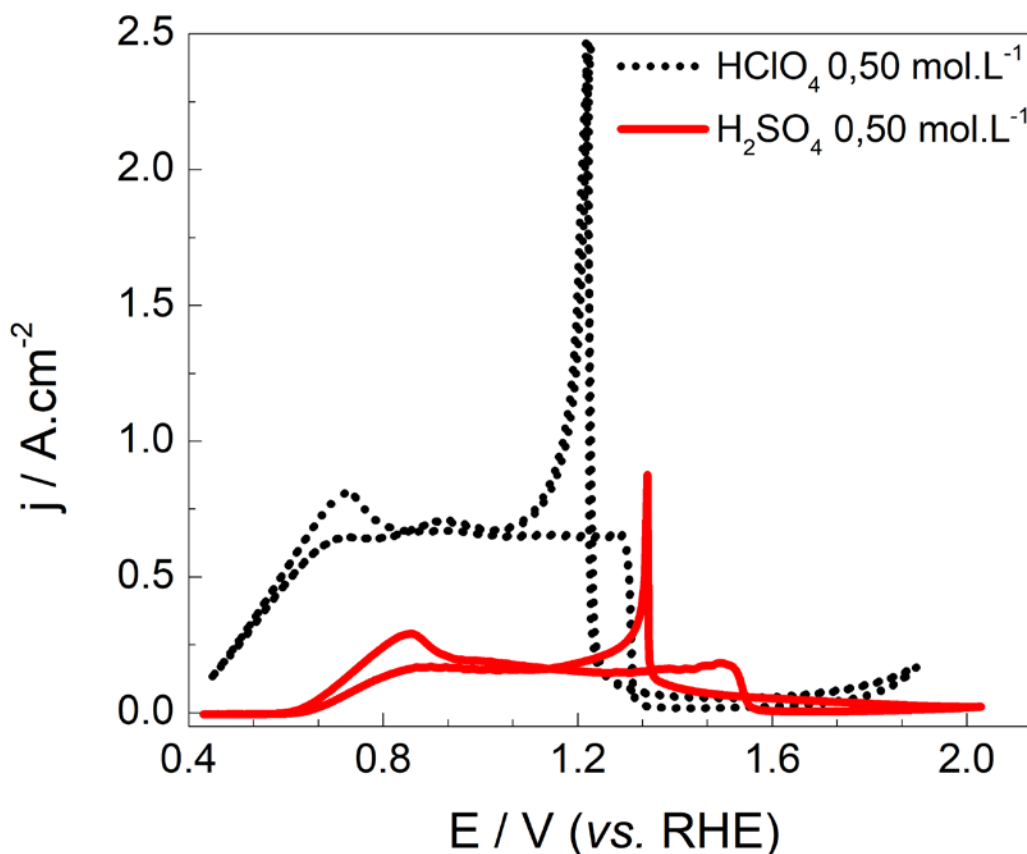


Figure 2. j/E Profiles for SO₂ in HClO₄ (doted black line) and H₂SO₄ (full red line) 0.50 mol.L⁻¹ on Au, at 0.10 V.s⁻¹.

Comparing both voltammetric profiles shown in Figure 2, two main points must be highlighted: (i) the SO₂ oxidation starts at less positive potentials in HClO₄ than in H₂SO₄ and (ii) the current

density is significantly higher in HClO_4 than in H_2SO_4 . Evidently, anion adsorption is a key point for this whole process and, even though from the practical point of view the use of sulfuric acid is compulsory, some fundamental understanding can be reached by studies in the presence of ClO_4^- anions, which only weakly interact with Au surfaces¹⁹.

Despite the fact that the potential window and current intensity are different in both electrolytes, the j/E profiles are quite similar. In both electrolytes, regions of bi-stability can be found, i.e. two different states are stable and coexist in the same potential window (1.15 – 1.50 V_{RHE} for H_2SO_4 and 1.00 – 1.30 V_{RHE} for HClO_4). To investigate the reaction in these potential regions further, potential step techniques (Figure 3) were applied. It was found that in the presence of the chaotrophic anion ClO_4^- damped current oscillations occur when the potential was stepped from open circuit potential (OCP) to the bi-stable potential region (1.00 - 1.30 V_{RHE}); a phenomena which so far has not been reported for this process^{6-8,17,18,20}. Stepping the potential to a value of 1.00 V_{RHE} , the current first oscillates and then adjusts to a fixed value. By comparison a potential step to 1.30 V_{RHE} leads to a current drop to zero after a few seconds, see Figure 3A. This behaviour can be explained by the generation of species that poison the reaction by strongly bonding to the Au surface. On the other hand, in the presence of HSO_4^- , a kosmothropic anion, only an irregular current behavior is observed, but no clear oscillations, see Figure 3B.

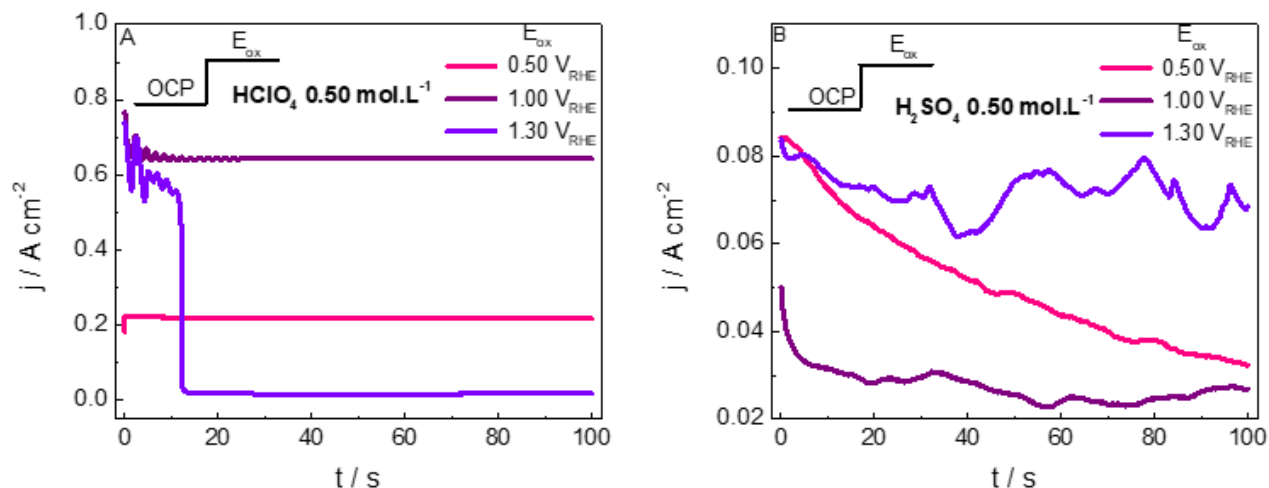


Figure 3. j/t current transients for oxidation of SO_2 on Au surface in HClO_4 0.50 mol L^{-1} (A) and H_2SO_4 0.50 mol.L^{-1} (B). The electrode potential is stepped from open circuit potential (OCP) to the potentials indicated in the figure.

Current oscillations of SO_2 oxidation systems were reported previously by O'Brein *et al.*^{12,13}, also observing an oscillatory behavior under potentiostatic mode for Pt electrodes modified with a thin layer of S atoms. The authors report that these oscillations are clearly observed in H_2SO_4 supporting electrolyte, but only in high concentrations, indicating that the oscillatory behavior is related to the SO_2 - HSO_4 interaction¹³.

In the present work neither any kind of pre-treatment was performed nor was the H_2SO_4 concentration increased. The fact that no oscillations were observed in H_2SO_4 solution is a strong indication that a different pathway must be involved, probably related to the nature of the electrode surface, endorsing the non-expected oscillatory behavior observed for gold/ HClO_4 system (Figure 3A).

For further investigation and characterization of this oscillatory behavior, galvanostatic experiments were carried out as well, see Figure 4. As result of the different current densities observed in the potentiostatic measurements (Figure 2), first the current densities have to be adjusted for both electrolytes.

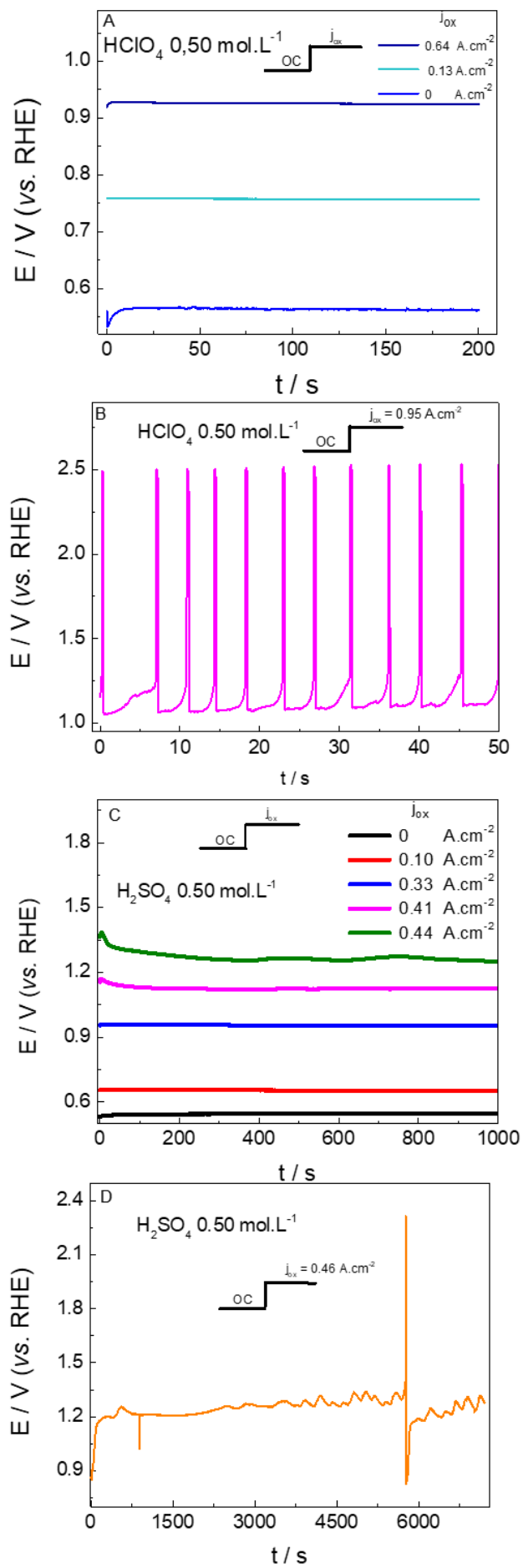


Figure 4. E/t profiles for selected current densities (shown) for SO₂ oxidation in HClO₄ (**A**, **B**) and H₂SO₄ (**C** and **D**) 0.50 mol L⁻¹.

Figure 4A demonstrates that increasing the current density in 0.50 mol L⁻¹ HClO₄, the electrode potential remains stable until 0.64 A cm⁻², whereas at 0.95 A cm⁻² potential oscillations are observed, see Figure 4B. In this condition, the potential sharply increases from 1.00 V_{RHE} to *ca.* 2.5 V_{RHE} diminishing steeply to 1.00 V_{RHE}, starting a periodic oscillating behavior. The potential where the oscillations begin (1.00 V_{RHE}) is less positive than the potential where Au oxidation takes place, but lies within the potential region where two states can coexist, as mentioned before and depicted in Figure 2. The j/E profile in Figure 2 shows a current increase at *ca.* 1.90 V_{RHE}, due to the O₂ evolution reaction; this indicates that the potential oscillations depicted in Figure 4B occur in the potential region between the generation of species that poison the reaction (Figures 2 and 3A) and the O₂ evolution. This observation indicates that the oscillatory behavior is caused by cycles of blocking-cleaning of the surface, *i.e.* the “poison” blocks the surface, decreasing the electrode activity and consequently the electrode potential sharply increases. This “poison” was suggested by O’Brien *et al.*^{12,13} as being the anion S₂O₆²⁻, a non-electroactive species that should increase the electrode resistance. The authors discuss the anion as a possible explanation for the observed current oscillations, classified as a negative differential resistor (NDR) type¹². This species is reported in the literature to be involved in other oscillatory behavior, such as chemical degradation of thiosulfate²¹, bisulfite²² and electrochemical degradation of thiosulfate^{23,24}, all presenting oscillations.

When the electrode reaches the potential for O₂ evolution, the “poison” is removed and the surface is cleaned. This increases the activity and the electrode potential drops back to 1.00 V_{RHE}, where the cycle restarts. Interestingly, no oscillations are observed in H₂SO₄, see Figures 4C – D. The

electrode potential stabilizes at values more positives than 1.15 V_{RHE} in the potential window where the sharp peak is observed in the cyclic voltammogram of Figure 2.

The NDR oscillatory behavior, suggested by O'Brien *et al.*^{12,13} would not explain the potential oscillations observed in Figure 4B, since this kind of behavior involves the presence of a single blocking species^{25,26}. The presence of potential oscillations are related to a hidden negative differential resistor (HNDR)²⁵ expecting the oscillations to be related not just to one but to two blocking species, as it was suggested for formic acid in alkaline conditions²⁵. Considering this, it is possible to infer that there are competing poisonous species for the adsorption sites of the electrode surface avoiding S₂O₆²⁻ to be assumed the only responsible for the oscillations. As a consequence, the differential equation to model the system should be much more complex.

CONCLUSIONS

Since SO₂ adsorption has to occur in the first step of the oxidation mechanism, the competition for adsorption sites between the electroactive species and the kosmotropic anion (HSO₄⁻) must play an important role for avoiding the bifurcation to occur; the adsorbed anions probably block the surface not enabling the critical amount of intermediates to be reached. On the contrary, in the presence of the chaotropic anion (ClO₄⁻), which does not strongly adsorb at the surface, bifurcation conditions are reached leading to an oscillatory behavior.

It is therefore concluded that the observed reaction mechanism on Au is significantly different than the one observed on Pt; not in agreement neither with predictions from theoretical calculations⁹ nor with other pathways suggested¹³. On Au, a much more complex mechanism is observed with bifurcation occurring in the presence of a chaotropic anion that lead to a larger number of sites available for SO₂ adsorption. These oscillations can be also interesting from the

economical point of view, since they can avoid the poisoning of the electrode allowing the system to be used for longer time.

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